## A Pyridyltriazol Functionalized Zirconium Metal-Organic Framework for Selective and Highly Efficient Adsorption of Palladium

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DMSO-*d*<sub>6</sub>/HF<sub>aq</sub> mixture.



**Figure S2.** Expanded <sup>1</sup>H NMR spectrum (between 6.6-11.6 ppm) of the digested UiO-66-NH<sub>2</sub> synthesized according to Corma method in a DMSO- $d_6$ /HF<sub>aq</sub> mixture.



<sup>13.0</sup> <sup>12.5</sup> <sup>12.0</sup> <sup>11.5</sup> <sup>11.0</sup> <sup>10.5</sup> <sup>10.0</sup> <sup>9.5</sup> <sup>9.0</sup> <sup>8.5</sup> <sup>8.0</sup> <sup>7.5</sup> <sup>7.0</sup> <sup>6.5</sup> <sup>6.0</sup> <sup>6.5</sup> <sup>5.5</sup> <sup>5.0</sup> <sup>4.5</sup> <sup>4.0</sup> <sup>3.5</sup> <sup>3.0</sup> <sup>2.5</sup> <sup>2.0</sup> <sup>1.5</sup> <sup>1.0</sup> <sup>0.5</sup> **Figure S3.** <sup>1</sup>H NMR spectra of digested sample of UiO-66-NH<sub>2</sub> after refluxing in MeOH for 48 h (pure UiO-66-NH<sub>2</sub> MOF).



**Figure S4.** <sup>1</sup>H NMR spectrum of the digestion of UiO-66-N<sub>3</sub> in a DMSO- $d_6$ /HF<sub>aq</sub> mixture (The amount of azide-functionlized MOF could be calculated about 95% (UiO-66-N<sub>3</sub>/NH<sub>2</sub>(95/5)).



**Figure S5.** <sup>1</sup>H NMR spectrum of the digestion of UiO-66-Pyta in a DMSO- $d_6$ /HF<sub>aq</sub> mixture (The amount of Pyta-functionlized MOF could be calculated about 24% (UiO-66-N<sub>3</sub>/NH<sub>2</sub>/Pyta(95/5/24)). This multifunctional MOF was called UiO-66-Pyta.



Figure S6. TGA profiles of a) UiO-66-Pyta, and b) UiO-66-Pyta-Pd



Figure S7. Zeta potential of UiO-66-Pyta at different pH values.



Figure S8. Effect of amount of adsorbent on the extraction recovery of palladium ions.



**Figure S9.** SEM images of pyridyltriazol-functionalized UiO-66 (UiO-66-Pyta) particles 60-75 nm in size (Preparation: Zirconium(IV) chloride (0.4 g, 1.7 mmol) was dissolved in DMF (75 mL) at 55  $\pm$  5 °C and acetic acid (1.425 mL) was added. 2-Aminoterephthalic acid (0.311 g, 1.7 mmol) was dissolved in DMF (25 mL) and then was added to the clear solution. Afterwards, water (0.125 mL, 0.007 mmol) was added to the solution. The capped vial was sonicated at 60 °C and placed in a bath at 120 °C for 14 h. After cooling to room temperature, the precipitate was isolated by centrifugation and washed with DMF, and EtOH several times. Finally, the solid was dried under reduced pressure (80 °C, 3 h) to give the UiO-66-NH<sub>2</sub> MOF. The sample was then subsequently used for synthesis of the UiO-66-Pyta MOF as mentioned in the experimental section, see section of synthesis of the MOFs).



Figure S10. Effect of eluent concentration on the extraction efficiency of palladium ions.

**Table S1.** Tolerance limits of MOF adsorbent in the detection of  $0.1 \text{ mg } \text{L}^{-1}$  palladium ions.

Tolerance limit for cations (mg L <sup>-1</sup> ) in sample solution													
Li+	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	$Mg^{2+}$	$Zn^{2+}$	$Pb^{2+}$	Fe <sup>3+</sup>	$Mn^{2+}$	Ni <sup>2+</sup>	Co <sup>2+</sup>	$Al^{3+}$	Cu <sup>2+</sup>	$Ag^+$
5.0	5.0	5.0	5.0	5.0	2.0	1.5	2.0	2.0	2.0	2.0	1.5	2.0	2.2



Figure S11. Effect of salt addition on the extraction efficiency of palladium ions.



Wavenumber (cm<sup>-1</sup>)

Figure S12. FT-IR spectra of UiO-66-Pyta a) before (bottom), and b) after Pd loading (top).



**Figure S13.** PXRD patterns of a) UiO-66-Pyta, b) Pd loaded UiO-66-Pyta (Adsorption experiment, UiO-66-Pyta-Pd), and c) UiO-66-Pyta-Pd treated with  $HNO_3$  (Pd desorption from UiO-66-Pyta-Pd towards regenerating UiO-66-Pyta).



**Figure S14.** SEM images of a) UiO-66-Pyta-Pd (adoption experiment) and b) UiO-66-Pyta-Pd after Pd extraction (desorption experiment, Desorbed MOF).

![](_page_13_Figure_0.jpeg)

**Figure S15.** Energy-dispersive X-ray (EDS) analysis of the Pd loaded UiO-66-Pyta (The analysis of UiO-66-Pyta-Pd showed that Pd certainly adsorbed on the MOF).

![](_page_14_Figure_0.jpeg)

**Figure S16.** XPS pattern of UiO-66-Pyta-Pd(II) showing the Pd 3d region with the corresponding best fit to individual component.

![](_page_14_Figure_2.jpeg)

![](_page_15_Figure_0.jpeg)

Figure S17. XPS patterns of UiO-66-Pyta and UiO-66-Pyta-Pd showing the N 1s and O 1s regions.

![](_page_15_Figure_2.jpeg)

Scheme S1. Suzuki-Miyaura cross-coupling reaction using UiO-66-Pyta-Pd as catalyst.

Run <sup>b</sup>	1	2	3
Yield	80	80	79

Table S2. Recyclability of the UiO-66-Pyta-Pd catalyst.<sup>a</sup>

<sup>a</sup> Conditions: Bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (10 mg),  $K_2CO_3$  (2 mmol) in EtOH (6 mL), T = 80 °C, 2 h.

<sup>&</sup>lt;sup>b</sup> After each run, the catalyst was removed from the solution by centrifugation and washed with ethyl acetate and methanol and then soaked in methanol at  $\sim$ 50° C for 3 h. Finally, the solid was washed by methanol and acetone and then activated at 90 °C for 3 h under vacuum before the next run.

![](_page_16_Picture_0.jpeg)

Figure S18. SEM images of the reused UiO-66-Pyta-Pd.

![](_page_17_Figure_0.jpeg)

Figure S19. <sup>1</sup>H NMR spectrum of the product in CDCl<sub>3</sub>.